

# Size, Shape and Flow of powders for use in Selective Laser Sintering (SLS)

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**ABSTRACT:** This paper investigates the effects of particles size and morphology on flowability of a range of polymeric powders (SLS and non-SLS grades). The effect of additives incorporation, as well as drying or sieving, on the flowability characteristics of the powders is also analyzed. The results show that the particle morphology has a stronger influence on the flowability than the particle size distribution. Moreover, the incorporation of additives has to be carefully considered in order to have positive effects on the powder flowability.

## 1 INTRODUCTION

Selective Laser Sintering is one of the additive layer manufacturing (ALM) technologies capable of building layer upon layer three dimensional objects by selectively sintering powder materials. Over the years, most polymeric SLS research focused either on the manufacturing process or on the characterization of the final sintered parts. Very little attention is being given to the morphology of powder materials and their influence on the sintering process and ultimately the part properties (Zarringhalam, Hopkinson et al. 2006; Goodridge, Hague et al. 2010). Whereas the behavior of polymeric powders has been fully investigated for other conventional manufacturing process such as rotational molding, cold compaction (Truss, Han et al. 1980; Olinek, Anand et al. 2005), analysis into the optimum properties of SLS powders is missing. Therefore the aim of this paper is to investigate the behavior of various powders with particular attention to their ability to flow. Flowability plays a key role in the SLS process as the lack of homogeneous and even layers leads to porous, weak SLS parts. Flowability depends on several factors: powder itself (particle size distribution, particle shape), the environmental conditions (temperature, moisture) and according to some authors the test conditions (Prescott J.K. 2000; Schulze 2006-2011). Schulze(2006-2011) reported basic concepts about bulk solid materials and flowability and he described the main physical factors affecting flowability such as adhesive strength and wall friction. Prescott and Bar-

num (2000) suggest distinguishing between “powder flow properties” and “powder flowability”. Powder flow properties are the properties due to the interactions between the individual particles which affect the flow performance: powder density, compressibility, cohesive strengths within the particles and wall friction. Powder flowability instead refers to how a given material will flow in specific equipment, implying that the same material will behave differently in different flow equipment conditions. In this scenario they largely recommend to use a test able to simulate as closely as possible the flow in the equipment wherein one is interested. Wu et al.(2006) studied the flow of a 90µm average size irregular steel powder experimentally and numerically in different conditions: presence of lubricants, air and vacuum environment. According to their simulations, particle materials can be divided into two groups: particles with shapes that allow tessellating (rectangular and hexagonal) and non-tessellating particles. The first group exhibits a lower flowability and they state that the presence of air during a flow process complicates the flow patterns. Yang et al.(2007) review the common features of powder that affect flowability. Interesting remarks are: high sphericity of particle leads to better flow performances; coarse powders flow easier than fine powders; electrostatic forces, temperature and humidity affect the flow. The electrostatic forces come from impurities, crystalline defects, and absorption of gas on the crystals. Humidity is responsible for charging electrostatically the particles. At high relative humidity, all particles tend to charge negatively, at low relative humidity coarse powders tend

to charge positively and fine particle negatively. Van Der Schueren et al. (1995) analyzed three deposition methods in selective metal sintering. They state that the flow is mainly influenced by the inter-particle friction. The spherical shape of particles ensures the minimal contact between particles causing a reduction in friction. Lastly, Amado et al. (2011) focused on the characterization of powder for Selective Laser Sintering. Powders were characterized by using an image-based powder analyzer system formed by a rotational drum and image acquisition system. By recording the powder free surface and the cross sectional area of powder inside the drum, the material is analyzed in terms of flow and fluidized behaviors. The indexes used were: avalanche angle, surface fractal, volume expansion ratio, fluidized volume slope, fluidized height slope and final settling time. They examined nine types of materials of different chemical nature, compounding, obtained by different methods with heterogeneous and homogenous mixed phases. According to the authors, the advantage of this instrumentation is that the rotational drum can be set at the same speed performed in the SLS machine from Sinterstation and EOS.

## 2 EXPERIMENTAL WORK

### 2.1 Materials

The materials analyzed in this study can be divided into three groups: SLS powder grades (EOS HP3, EOS PA2200(EOS)), non-SLS grades (PEEK-OPTIMA® polymer supplied by Invibio® Biomaterial Solutions (Invibio)) and additives (glass, hydroxyapatite, calcium carbonate). EOS HP3 is a high temperature thermoplastic, belonging to the family of polyaryletherketones (PAEKs), known for its high mechanical properties, elevated thermal stability and outstanding chemical resistance. Nylon 12 named EOS PA2200 is a well-established SLS material and highly recyclable. A mixture of 50% virgin and 50% used material was used. Such grades were compared to the performance of PEEK-OPTIMA®, another high temperature thermoplastic polymer belonging to PAEKs, but chemically different and highly biocompatible. The glass powder is a SLS grade powder known under the trade name of Spherglass 2000 (supplied by Potters). Spherglass 2000 was studied individually and as an additive in combination with the other powders. Other additives include Hydroxyapatite (HA) (supplied by Sigma-Aldrich) and Calcium carbonate ( $\text{CaCO}_3$ ) (supplied by Ash Grove Cement Company, KS). Hydroxyapatite was chosen because of its biocompatible and bioactive characteristics, and therefore well-designed for biomedical ap-

plications. Calcium Carbonate was selected due to its small particle size and wide distribution. The following mixtures were prepared by weight: 10% Spherglass 2000 + 90% PEEK-OPTIMA®; 20% Spherglass 2000 + 80% PEEK-OPTIMA®; 30% Spherglass 2000 + 70% PEEK-OPTIMA®; 20% HA+ 80% PEEK-OPTIMA®; 30% HA + 70% PEEK-OPTIMA®; 10%  $\text{CaCO}_3$  + 90% PEEK-OPTIMA®; 20%  $\text{CaCO}_3$  +80% PEEK-OPTIMA® and 30%  $\text{CaCO}_3$ + 70% PEEK-OPTIMA®.

### 2.2 Particle Size Distribution (PSD)

The particle size distributions of powder materials and additives were performed on the particle sizing instrument Saturn DigiSizer 5200, Micrometrics. The instrument gives the particle size distribution of a sample by detecting its light scattering pattern when the specimen is suspended in a specific solution. Here, a solution of 0.4% sodium hexametaphosphate (more precisely, 6.7g sodium hexametaphosphate and 1.3g sodium hydrogen carbonate for 2L deionized water) was used. The tests were repeated three times on each sample and the average results of the three repeats are later reported.

### 2.3 Scanning Electron Microscopy (SEM)

SEM examination of all the powder materials was carried out by using a Hitachi S-3200N scanning electron microscope. The samples were coated with 4nm of gold coating in order to reduce the surface charging and the electron secondary imaging was set with an accelerating voltage of 25kV.

### 2.4 Particle Shape analysis

The shape analysis was carried out by using the image processing program Image J, software capable of evaluating shape descriptors on specimen images. SEM images were used and processed according to the following procedure: setting of the scale, conversion to binary image, drawing the edges of particles using the automatic wand and freehand tool, evaluation of the shape parameters through the ROI manager window (Fig.1). The particles analyzed were not overlapping and not lying on the edges of the image.

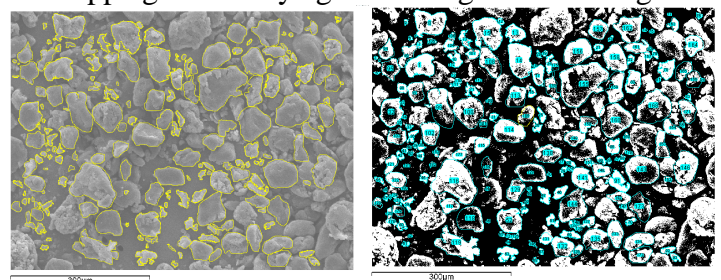


Figure 1. Shape analysis by IMAGE J

## 2.5 Angle of Repose test (AOR)

Angle of Repose (AOR) is a single-point test which quantifies the angle of a cone of bulk material over a flat surface assuming that each material has its own specific angle of repose. The cone is formed by dropping the material through a funnel of standardized dimensions and the angle considered is the inner one formed between the slant height and the horizontal plane. The smaller the angle of repose is, the higher the flowability is. The test was designed by following the ASTM C144 standard. However, some modifications were introduced: the use of a sheet of paper placed in the glass funnel in a way to fit perfectly the angle of the funnel and to facilitate the flow of powder; as the powders did not flow through the funnel if the funnel was completely filled, the powders were added in small amounts; the powder was supplied through the funnel until the cone of deposited material reached the tip of the nozzle. The test was repeated six times on each material.

## 3 RESULTS AND DISCUSSION

### 3.1 Particle Size analysis

The particle size distributions (PSD) of SLS grade powders (EOS HP3, EOS PA2200) and non SLS one (PEEK-OPTIMA®) are reported in figure 2. EOS HP3 and PEEK-OPTIMA® exhibit close PSDs, while EOS PA2200 curve is shifted, slightly indicating the presence of particles with higher dimensions than the ones contained in the other two grades. PSD data of additives for PEEK-OPTIMA® are showed in figure 3. The materials show quite different compositions. Calcium Carbonate results being constituted of a fairly constant amount of particles along all the particle dimensions. HA shows a bimodal distribution with peaks for dimensions at which PEEK-OPTIMA® shows fewer amounts of particles. Spherglass 2000 presents a similar PSD to the one of PEEK-OPTIMA® with a higher content of particles with smaller dimensions.

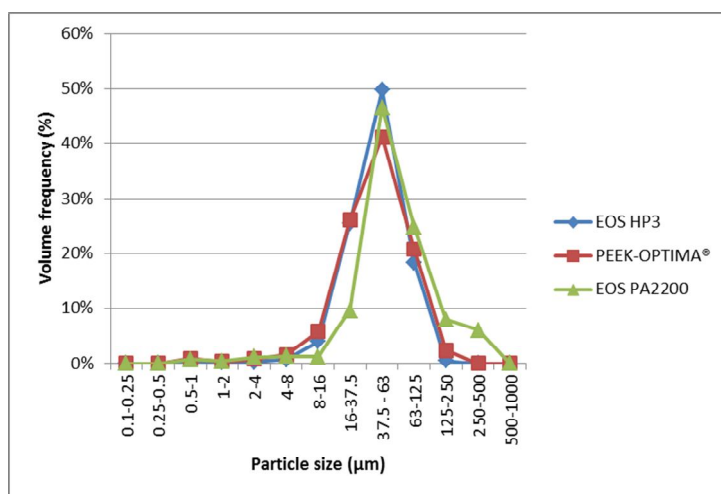


Figure 2. PSD of EOS HP3, EOS PA2200 and PEEK-OPTIMA®

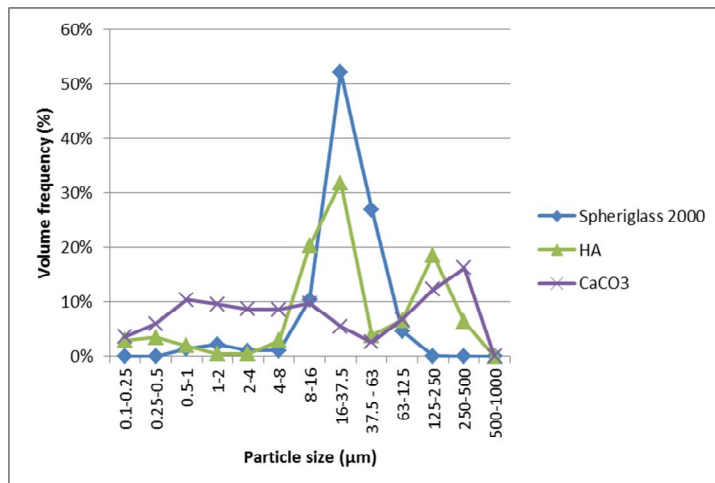


Figure 3. PSD of Spherglass 2000, HA and CaCO<sub>3</sub>

### 3.2 Particle Morphology results

#### 3.2.1 Particle Shape analysis

The shape analysis was carried out on EOS HP3 and PEEK-OPTIMA® grades. The number of particles evaluated was 1184 and 1167, respectively. The values obtained for the shape descriptor Roundness are reported (Fig. 4-5). Roundness is the ratio between the measured area of a particle and the area of an equivalent circle with the maximum length of the particle as diameter. Although the roundness range covered by EOS HP3 and PEEK-OPTIMA® is approximately the same, the PEEK-OPTIMA® particles have a slightly higher intensity of particles with low and middle range which suggests a higher surface area to the detriment of a round shape.

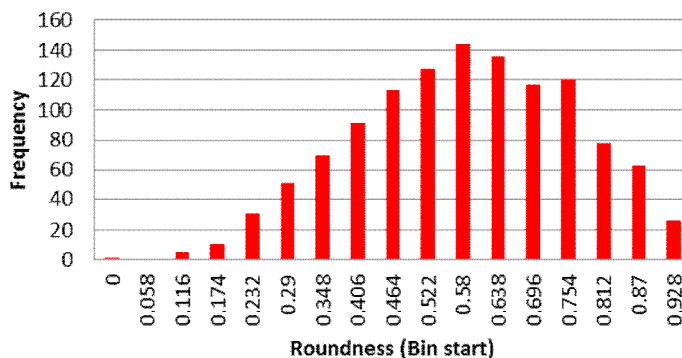


Figure 4. Roundness of EOS HP3



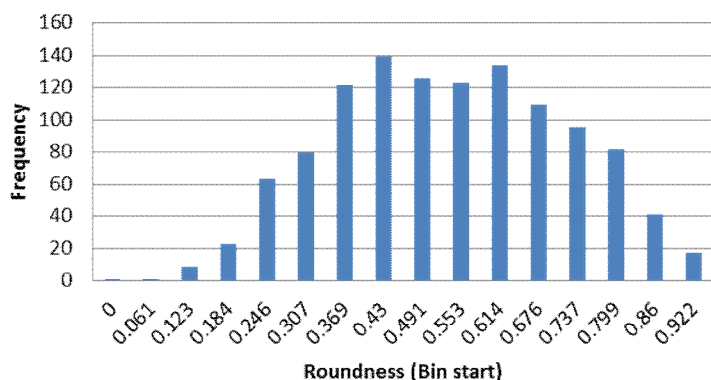


Figure 5. Roundness of PEEK-OPTIMA®

### 3.2.2 SEM of SLS and non-SLS powders

Particle morphology of EOS HP3 powder at different orders of magnification is reported in figures 6 and 7. EOS HP3 particles appear round with very smooth surfaces and a fully dense bulk. EOS PA 2200 particles are showed in figures 8 and 9. These particles look round with smooth but cracked surface probably due to the presence of used fraction. PEEK-OPTIMA® particles (Figs 10, 11) exhibit more angular shapes with particles having highly irregular structures with flakes on the surfaces. Such feature did not appear in the values of Roundness from the shape analysis in Image J as the software cannot pick up on surface irregularities if they do not lie on the external edge of a particle (Fig.12). Moreover PEEK-OPTIMA® particles are not fully dense.

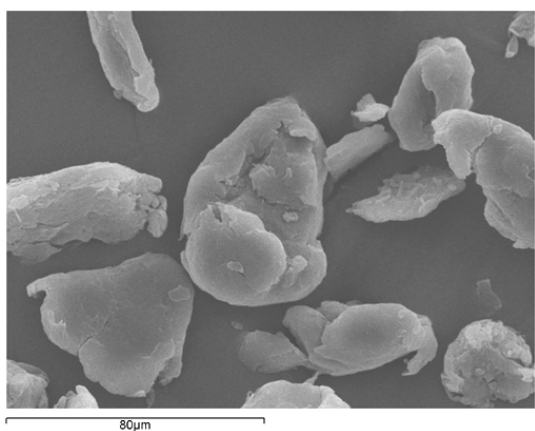


Figure 6. EOS HP3 at medium magnification

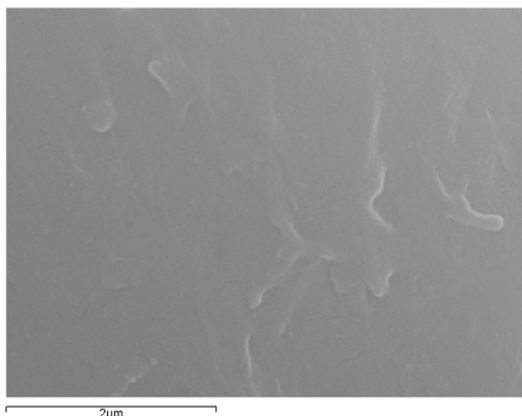


Figure 7. EOS HP3 at high magnification



Figure 8. EOS PA2200, medium magnification

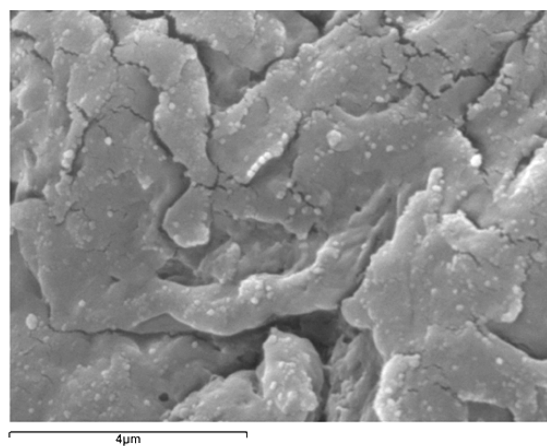


Figure 9. EOS PA2200, high magnification

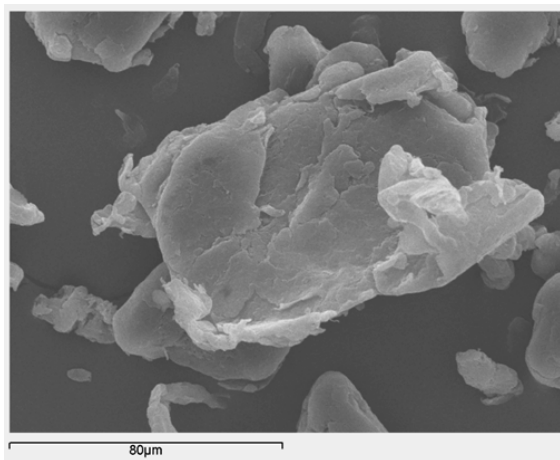


Figure 10. PEEK-OPTIMA®, medium magnification

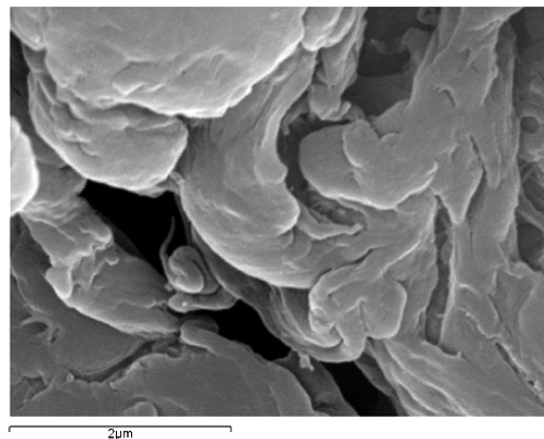


Figure 11 PEEK-OPTIMA®, high magnification

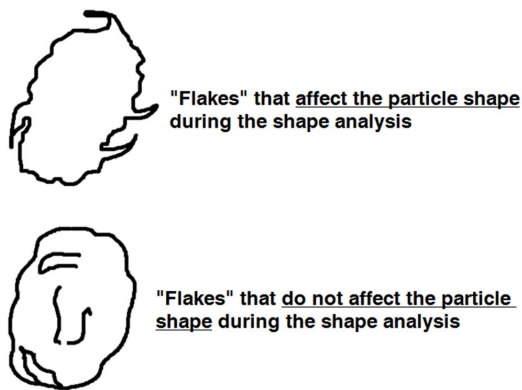


Figure 12. Flakes on Particle Surfaces and Shape

### 3.2.3 SEM of additives

Spheriglass 2000 particles are mostly round, smooth and dense. HA particles are round with quite complex nano-structures (Fig. 13), particles of Calcium Carbonate (Fig. 14) as noticed also from the PSD, are much smaller than the SLS powder grades or the additive powders and they seem to agglomerate.

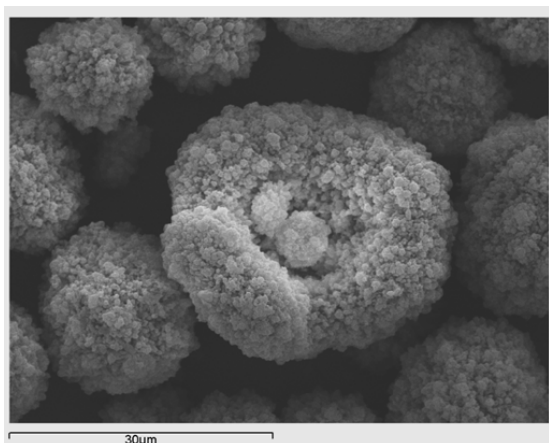


Figure 13. HA medium magnification

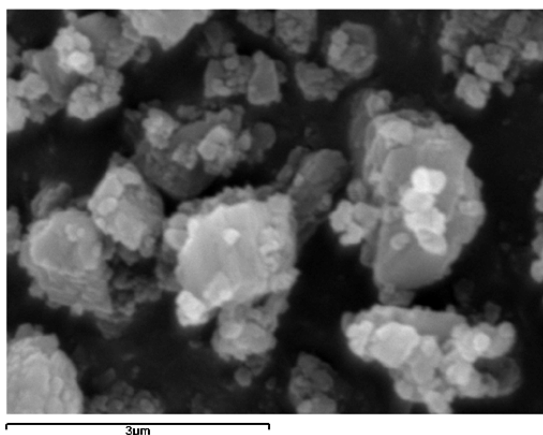


Figure 14. CaCO<sub>3</sub>, high magnification

### 3.3 Flowability results

The AOR values of all powders, SLS and non-SLS grades and their related mixtures are reported in table 1.

Table 1 AOR results

Materials	Angle of Repose (°)
Spheriglass 2000	23.6 ± 1.3
EOS PA2200	38.4 ± 0.8

EOS HP3	42.4 ± 1.1
PEEK-OPTIMA®	52.8 ± 0.9
PEEK-OPTIMA® + 20% HA	49.2 ± 1.0
PEEK-OPTIMA® + 30 %HA	50.4 ± 0.7
PEEK-OPTIMA® + 10% CaCO <sub>3</sub>	50.3 ± 1.0
PEEK-OPTIMA® + 20% CaCO <sub>3</sub>	49.4 ± 0.7
PEEK-OPTIMA® + 30% CaCO <sub>3</sub>	48.2 ± 1.0
PEEK-OPTIMA® + 10% Spheriglass 2000	51.8 ± 0.8
PEEK-OPTIMA® + 20% Spheriglass 2000	50.0 ± 0.9
PEEK-OPTIMA® + 30% Spheriglass 2000	48.6 ± 1.7

As expected, the AOR values are lower (higher flow-ability) for high spherical powder such as Spheriglass 2000 and for the SLS powder grades such as PA2200 and EOS HP3. PEEK-OPTIMA® powder presented the highest AOR value, which is representative of a poor flow material. This is not surprising considering the particle morphology noticed during the SEM analysis. Several studies in the literature (Tan, Chua et al. 2003; Pohle, Ponader et al. 2007; Schmidt, Pohle et al. 2007; von Wilmowsky, Vairaktaris et al. 2008) discuss the incorporation of additives to improve the flow of new powders for SLS applications. In most cases, the addition of small quantities of powders seems to improve flowability although the mechanisms leading to this improvement are never discussed and no results are presented to support their proposals. The authors here believe that depending on the particle size, these additives can either simply help the main polymeric powder flow by interaction with similar size spherical particles or the additives has such a small particle size that they fill in the spaces between the flakes and the main body of the particle, leading to less interactions/agglomerations of the particles and therefore better flow. Such hypothesis is supported by showing the mixture of 30 % CaCO<sub>3</sub> + 70% PEEK-OPTIMA® (Fig.15). The smaller particles of CaCO<sub>3</sub> are placed on the empty spaces created by the flakes on the surfaces of the PEEK-OPTIMA® particles, making them rounder overall. It is believed that the flakes help the particle interlock and drag each other into agglomerates and spread poorly.

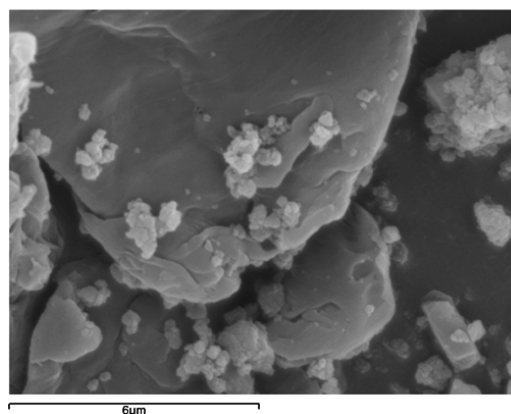


Figure 15. 30%CaCO<sub>3</sub> + 70% PEEK-OPTIMA®

Adding the glass particles to PEEK-OPTIMA® caused a slight decrease in the AOR value and therefore an increase of the flowability, as expected from the corresponding SEM images. Similarly, the addition of HA particles to PEEK-OPTIMA® improved the flow property only at the lowest concentration (20%). This may be because of the complex structure of HA particles, which instead of facilitating reciprocal sliding of the particles, caused more inter-particle mechanical locking. In both cases, glass and hydroxyapatite, it was surprising to see that these particles although round do not necessary help the flow in spite of their high concentrations in the mix. Interestingly, the addition of CaCO<sub>3</sub> powder makes the polymeric powder flow best, increase of concentration leading to a lower AOR and therefore better flow. The AOR values have also been carried out on the dried and sieved EOS HP3 and PEEK-OPTIMA® grades in order to investigate the effect of water adsorption and narrow particle size distribution, respectively. The powders have been dried in an air circulating oven at a temperature range of 140-160 °C for 21-22 hours. Sieving was carried out to get sample with a final maximum size of 90 microns. Results are reported in table 2.

Table 2 AOR results of dried and sieved materials

Materials	Angle of Repose (°)
EOS HP3	42.4 ± 1.1
PEEK-OPTIMA®	52.8 ± 0.9
Dried EOS HP3	40.1 ± 0.7
Dried PEEK-OPTIMA®	51.6 ± 1.0
Sieved EOS HP3	41.3 ± 0.6
Sieved PEEK-OPTIMA®	50.3 ± 1.0

The results obtained showed that both drying and sieving slightly improve the AOR values.

## CONCLUSIONS

Although the PSD results revealed similar trends for the SLS and non-SLS powder grades, the angle of repose led to very different findings. The AOR for the SLS grades was calculated between 38 and 42, where the non-SLS grade recorded a much higher AOR, 52. A closer SEM analysis showed morphological differences between the grades and explained the large differences in AOR. The presence of additives, just slightly improved the AOR independent of their particle size distribution. Similarly, drying or sieving of particles does not impact significantly on the powder flowability. This study shows the importance of particle analysis in the SLS process. Presence of angular particles, particles with flakes on the surface, or particles with less dense structures can easily lead to weak parts, with high porosity.

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